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(54) 【発明の名称】 球状重合体粒子の製造方法

(57) 【要約】

【目的】 真球状でかつ粒径が250 $\mu$ m $\sim$ 2mmの間で粒度分布を有するメタクリル酸エステル重合体粒子を工業的にかつ収率よく製造する方法を提供する。

【構成】 水性媒体中に部分けん化ポリビニルアルコール及び硫酸銅を溶解した分散安定剤の存在下、メタクリル酸メチルモノマーを懸濁重合させて大粒径の真球状重合体の製法。

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又はメタクリレート、ジペンタエリスリトールヘキサアクリレート又はメタクリレート、ビスフェノールAのエチレンオキサイド又はプロピレンオキサイド付加物のジアクリレート又はメタクリレート、ハロゲン化ビスフェノールAのエチレンオキサイド又はプロピレンオキサイド付加物のジアクリレート又はメタクリレート、イソシアヌレート、トリアクリレート又はメタクリレート、イソシアヌレートのエチレンオキサイド又はプロピレンオキサイド付加物のジ又はトリアクリレート又はメタクリレート等の多価アクリレート類又はメタクリレート類；  
 トリアリルイソシアヌレート、ジアリルフタレート等の多価アクリレート類；更にグリシジルアクリレート又はメタクリレート、アクリルグリシジルエーテルやアクリル酸、メタクリル酸、イタコン酸、マレイン酸、フマル酸もしくはそれらの半エステル化物等が挙げらる。二官能性モノマーは、例えば、エチレングリコールジアクリレート、エチレングリコールジメタクリレート、トリエチレングリコールジメタクリレート、テトラエチレングリコールジメタクリレート、1, 3-ブチレングリコールジメタクリレート、トリメチロールプロパントリアクリレート、トリメチロールプロパントリメタクリレート、1, 4-ブタンジオールジアクリレート、ネオペンチルグリコールアクリレート、1, 6-ヘキサジオールジアクリレート、ペンタエリスリトールジアクリレート、ペンタエリスリトールトリアクリレート、ペンタエリスリトールジメタクリレート、ペンタエリスリトールトリメタクリレート、ペンタエリスリトールテトラメタクリレート、グリセロールジメタクリレート、グリセロールジアクリレート、グリセロールアリロキシジメタクリレート、1, 1, 1-トリスヒドロキシメチルエタンジアクリレート、1, 1, 1-トリスヒドロキシメチルエタントリアクリレート、1, 1, 1-トリスヒドロキシメチルエタンジメタクリレート、1, 1, 1-トリスヒドロキシメチルエタントリメタクリレート、1, 1, 1-トリスヒドロキシメチルプロパンジアクリレート、1, 1, 1-トリスヒドロキシメチルプロパントリアクリレート、1, 1, 1-トリスヒドロキシメチルプロパンジメタクリレート、1, 1, 1-トリスヒドロキシメチルプロパントリメタクリレート、トリアリルシアヌレート、トリアリルイソシアヌレート、トリアリルトリメテート、ジアリルテレフタレート、ジアリルフタレート等が挙げられる。これらの一官能性モノマー、二官能性モノマーは1種又は2種以上用いることができる。

【0006】本発明の重合モノマーであるメタクリル酸メチルの含有量は、重合体と構成するモノマー全体の10～100重量%である。10重量%未満では重合安定性及び粒径制御上好ましくない。メタクリル酸メチルが100重量%未満の場合は、前述の共重合可能なモノマーを90重量%未満添加する。この共重合可能なモノマーとして用

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いられる一官能性モノマーの添加量は90重量%未満、好ましくは50重量%以下であり、二官能性モノマーの添加量は50重量%以下、好ましくは10重量%以下である。

【0007】本発明に使用する分散安定剤の部分けん化ポリビニルアルコールはけん化度が100モル%でないポリビニルアルコールであり、好ましくはけん化度75モル%以上、更に好ましくは85モル%以上のものであり、4重量%水溶液の20℃の粘度が30cps以上のものである。完全けん化ポリビニルアルコールでは充分な効果を示さない。この部分けん化ポリビニルアルコールは重合モノマーに対し0.1～1重量%添加すると好結果が得られる。0.1重量%未満では重合系が不安定となり塊状凝集物が多量に発生し粒子の収率低下を招くおそれがある。また、1重量%を超えて添加しても安定性に影響はないが経済的に不利である。

【0008】本発明において添加される硫酸銅は5水和物として使用され、部分けん化ポリビニルアルコールに対し0.4～40重量%用いるのが有効である。0.4重量%未満では、余り効果は見られず、40重量%を超えて添加すると水溶液重合禁止作用が現われ重合率の低下を招くおそれがある。なお、硫酸銅以外の塩化鉄、硫酸ニッケル、硫酸マグネシウム等の金属化合物を添加しても本発明のような大粒子径の重合粒子は得られない。

【0009】本発明の懸濁重合は一般の懸濁重合法が採用される。一般的に懸濁重合を行う際には、凝集を防ぐために分散安定剤が用いられる。この分散安定剤は用いるモノマーの種類に応じて異なるが、例えば、バリウム、カルシウム、マグネシウムの硫酸塩、炭酸塩、リン酸塩、水酸化アルミニウム、水酸化マグネシウム等の難水溶性の無機塩または、ポリビニルアルコール、ポリアクリル酸、ゼラチン、ポリエチレングリコール、ポリアクリルアミド、カルボキシメチルセルロース等の水溶性高分子が用いられる。また、重合開始剤は、油溶性の開始剤を用い、ベンゾイルパーオキサイド、ラウリルパーオキサイドのような有機過氧化物、アゾビスイソブチロニトリル等のアゾ開始剤または、光重合や放射線重合も選択できる。開始剤類はあらかじめモノマーに加えられ、分散安定剤と共に必要量の水と混合される。このような重合系に機械的剪断力を加えることにより油滴を微細化させ、重合させる。

【0010】

【実施例】次に本発明を実施例によりさらに詳細に説明する。

【0011】実施例1

攪拌装置、温度計、窒素ガス導入管を有するステンレス製10l重合容器中に、水140重量部を仕込み、ポリビニルアルコール（クラレ製クラレポパールPVA-235、けん化度88%、20℃の粘度約90cps）0.33重量部（対モノマー0.55重量%）及び硫酸銅・5水和物0.012重量部（対PVA約3.6重量%）を溶解させた後、ベンゾイルパーオキ

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ッケル、硫酸マグネシウム等の金属化合物を添加しても

本発明のような大粒子径の重合粒子は得られない。

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## CLAIMS

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[Claim(s)]

[Claim 1] The manufacture method of the spherical polymer particle of 250 micrometers - 2mm of mean particle diameters of the polymer particle characterized by carrying out the suspension polymerization of the monomer which contains 10 - 100 % of the weight of methyl methacrylates, 0 - 90 % of the weight of 1 functionality monomers in which other polymerizations are possible, and 0 - 50 % of the weight of 2 functionality monomers in an aqueous medium under existence of the distributed stabilizer which dissolved partial saponification polyvinyl alcohol and the copper sulfate.

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[Translation done.]

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the method of manufacturing the particle whose mean particle diameter of the polymer particle used as the various pellets for molding, the sand for sandblasting, and a filler for optical diffusion is 250 micrometers - 2mm.

[0002]

[Description of the Prior Art] Conventionally, the polymer particle whose particle diameter is 250 micrometers - about 2mm and which becomes size comparatively has a latus use as the various pellets for molding, the sand for sandblasting, and a filler for optical diffusion. As the process of the polymer of such a particle that becomes size comparatively A vinyl system monomer in an aquosity solvent Poorly soluble mineral salt, alkyl naphthalenesulfonate, A polymerization is started under existence of a water-soluble metal salt. By adding a nonionic surface active agent, while a polymerization invert ratio is 55 - 75% The method (JP,4-22161,B) and styrene monomer which manufacture the vinyl system polymer particle whose mean particle diameter is 0.8-1.1mm, or the monomer in which styrene and copolymerization are possible The sodium of beta-naphthalenesulfonic acid formalin condensate or potassium salt, a calcium chloride, A suspension polymerization is indicated under existence of a phosphoric-acid tricalcium, and you add phosphoric-acid 3 sodium to this liquid between 15 - 50% of polymerization invert ratios, and make it react with a calcium chloride. and as basic calcium phosphate The method (JP,59-19125,B) of carrying out a polymerization succeedingly and manufacturing a with a particle size [ 460-1250micro ] styrene polymer particle is learned. Moreover, in case a polymer particle is manufactured according to a suspension polymerization, the method (JP,60-8302,A) of using the water-soluble-polymer matter as the method (JP,1-146910,A) of using water soluble polymers, such as polyvinyl alcohol and a polyacrylic acid, as a distributed stabilizer and a distributed stabilizer, and using a vanadium pentoxide and cupric chloride for this etc. is indicated.

[0003]

[Problem(s) to be Solved by the Invention] In the above-mentioned conventional method, when manufacturing a polymer particle with a comparatively big particle size, in order to prevent two-layer separation of the system of reaction by the method of adding a specific reagent in the fixed polymerization stage in polymerization progress of a monomer which requires difficult operation industrially and uses distributed stabilizers, such as polyvinyl alcohol of a JP,1-146910,A indication, and to equalize a system, it needs to be agitated more than fixed. In response to more mechanical shearing force, a particle diameter diameter[ of a granule ]-izes the oil droplet of a monomer in that case, and the polymer particle which is a particle diameter and which becomes size is not obtained. Moreover, in the method of a JP,60-8302,A indication, the copper chloride is added in the suspension polymerization, and this reagent acts as a polymerization inhibitor and has the trouble of polymerization degree not going up. using partial saponification polyvinyl alcohol and a copper sulfate as a distributed stabilizer, when carrying out the suspension polymerization of the methacrylic ester, in order that this invention may solve the fault of these conventional methods -- the conventional suspension-polymerization method -- if -- it aims at offering an advantageous manufacturing method industrially [ a large drop radial ball child's spherical polymer particle which was not obtained ]

[0004]

[Means for Solving the Problem] this invention persons – the above – as a result of repeating research about manufacture of the spherical polymer which canceled the fault of a well-known method, in the suspension polymerization of a methacrylic ester, by using a copper sulfate together with partial saponification polyvinyl alcohol, it knew that the large drop radial ball child of a spherical polymer could be manufactured, and this invention was completed That is, it is the manufacture method about the spherical polymer particle in the range of 250 micrometers - 2mm of mean particle diameters of a polymer particle by carrying out the suspension polymerization of the monomer which contains a methyl methacrylate ten to 100% of the weight under existence of the distributed stabilizer which dissolved partial saponification polyvinyl alcohol and a copper sulfate and 5 hydrate in the aqueous medium, and contains 0 - 90 % of the weight, and/or a 2 functionality monomer for the 1 functionality monomer in which other copolymerization is possible zero to 50% of the weight.

[0005] The 1 functionality monomer which is used for this invention and in which a methyl methacrylate and copolymerization are possible For example, an ethyl methacrylate, a methacrylic-acid propyl, a methacrylic-acid isopropyl, Methacrylic-acid butyl, a methacrylic-acid isobutyl, methacrylic-acid tertiarybutyl, A methacrylic-acid amyl, a methacrylic-acid isoamyl, methacrylic-acid 2-ethylhexyl, A methacrylic-acid desyl, methacrylic-acid lauryl, cyclohexyl methacrylate, The methacrylic esters which have the carbon numbers 1-18 of alkyl groups, such as a methacrylic-acid benzyl, methacrylic-acid 2-phenoxy ethyl, and methacrylic-acid 3-phenylpropyl; A methyl acrylate, An ethyl acrylate, an acrylic-acid propyl, an acrylic-acid isopropyl, A butyl acrylate, isobutyl acrylate, acrylic-acid tertiarybutyl, An acrylic-acid amyl, an acrylic-acid isoamyl, an acrylic-acid octyl, acrylic-acid 2-ethylhexyl, An acrylic-acid desyl, acrylic-acid lauryl, acrylic-acid cyclohexyl, The acrylic esters which have the carbon numbers 1-18 of alkyl groups, such as an acrylic-acid benzyl; Styrene, An alpha methyl styrene, PARAME chill styrene, vinyltoluene, isopropenyl styrene, Vinyl aromatic [ such as crawl styrene, ]; Acrylonitrile, a methacrylonitrile, Unsaturation nitril, such as ethacrylonitrile and phenyl acrylonitrile; Ethylene glycol diacrylate or methacrylate, Hexanediol diacrylate or methacrylate, a divinylbenzene, Trimethylolpropane triacrylate or methacrylate, BENTA erythritol tetraacrylate, or methacrylate, Diacrylate or methacrylate of the ethyleneoxide of dipentaerythritol hexaacrylate or methacrylate, and bisphenol A, or a propylene oxide addition product, Diacrylate or methacrylate of the ethyleneoxide of halogenation bisphenol A, or a propylene oxide addition product, The multiple-valued acrylate or methacrylate of the ethyleneoxide of the thoria chestnut rate of isocyanurate or methacrylate, and isocyanurate, or a propylene oxide addition product, such as II, a thoria chestnut rate, or methacrylate; Triallyl isocyanurate, Multiple-valued acrylate, such as a diallyl phthalate; glycidyl acrylate or methacrylate, acrylic glycidyl ether, an acrylic acid and a methacrylic acid, an itaconic acid, a maleic acid, fumaric acids, or those half-esterification objects mention further, and it is \*\*\*\*. A 2 functionality monomer For example, ethylene glycol diacrylate, Ethylene glycol dimethacrylate, triethylene-glycol dimethacrylate, Tetraethylene-glycol dimethacrylate, 1, 3-butyleneglycol dimethacrylate, Trimethylolpropane triacrylate, trimethylolpropanetrimethacrylate, 1, 4-butanediol diacrylate, neopentyl glycol acrylate, 1, 6-hexanediol diacrylate, pentaerythritol diacrylate, A pentaerythritol thoria chestnut rate, pentaerythritol tetraacrylate, Pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, Pentaerythritol tetrapod methacrylate, glycerol dimethacrylate, Glycerol diacrylate, glycerol aryloxy dimethacrylate, 1, 1, and 1-tris hydroxymethyl ethane diacrylate, 1 and 1, and 1-tris hydroxymethyl ETANTORI acrylate, 1, 1, and 1-tris hydroxymethyl ethane dimethacrylate, 1 and 1, and 1-tris hydroxymethyl ethane trimethacrylate, 1, 1, and 1-tris hydroxymethyl propane diacrylate, 1 and 1, and 1-tris hydroxymethyl PUROPANTORI acrylate, 1, 1, and 1-tris hydroxymethyl propane dimethacrylate, 1 and 1, and 1-tris hydroxymethyl propane trimethacrylate, A triaryl SHIANU rate, triallyl isocyanurate, triallyl trimellitate, diaryl terephthalate, a diallyl phthalate, etc. are mentioned. these 1 functionality monomers and a 2 functionality monomer – one sort – or two or more sorts can be used

[0006] The contents of the methyl methacrylate which is the polymerization monomer of this invention are a polymer and 10 - 100% of the weight of the whole monomer to constitute. At less than 10 % of the weight, it is not desirable on polymerization stability and particle-size control.

When a methyl methacrylate is less than 100 % of the weight, the monomer in which the above-mentioned copolymerization is possible is added less than 90% of the weight. The addition of the 1 functionality monomer used as a monomer in which this copolymerization is possible is 50 or less % of the weight preferably less than 90% of the weight, and the addition of a 2 functionality monomer is 10 or less % of the weight preferably 50 or less % of the weight.

[0007] the polyvinyl alcohol whose degree of saponification of the partial saponification polyvinyl alcohol of the distributed stabilizer used for this invention is not 100-mol % – it is – desirable – more than degree of saponification 75 mol % – it is a thing beyond 85 mol % still more preferably, and the viscosity of 20 degrees C of 4-% of the weight solution is a thing 30cps or more Effect sufficient in full saponification polyvinyl alcohol is not shown. A good result will be obtained if this partial saponification polyvinyl alcohol is added 0.1 to 1% of the weight to a polymerization monomer. At less than 0.1 % of the weight, a polymerization system becomes unstable and there is a possibility that a massive aggregate may occur so much and may cause the yield fall of a particle. Moreover, it is economically disadvantageous although it is uninfluential at stability even if it adds exceeding 1 % of the weight.

[0008] As for the copper sulfate added in this invention, it is effective for it to be used as five hydrates and to use 0.4 to 40% of the weight to partial saponification polyvinyl alcohol. At less than 0.4 % of the weight, not much, an effect is not seen, but when it adds exceeding 40 % of the weight, a possibility of an aqueous polymerization prohibition operation appearing and causing decline in conversion has it. In addition, even if it adds metallic compounds, such as ferric chloride other than a copper sulfate, a nickel sulfate, and magnesium sulfate, the polymerization particle of a large particle diameter like this invention is not obtained.

[0009] The suspension-polymerization method the suspension polymerization of this invention is general is adopted. In case a suspension polymerization is generally performed, a distributed stabilizer is used in order to prevent condensation. Although these distributed stabilizers differ according to the kind of monomer to be used, water soluble polymers, such as mineral salt of difficulty water solubility, such as a sulfate of barium, calcium, and magnesium, a carbonate, phosphate, an aluminum hydroxide, and a magnesium hydroxide, or polyvinyl alcohol, a polyacrylic acid, gelatin, a polyethylene glycol, a polyacrylamide, and a carboxymethyl cellulose, are used, for example. Moreover, a polymerization initiator can also choose an azo initiator, or photopolymerization and radiation polymerization, such as organic peroxide like benzoyl peroxide and lauryl peroxide, and an azobisisobutyronitril, using an oil-soluble initiator. Initiators are beforehand added to a monomer and it is mixed with the water of an initial complement with a distributed stabilizer. By applying mechanical shearing force to such a polymerization system, an oil droplet is made to turn minutely and carries out a polymerization.

[0010]

[Example] Next, an example explains this invention to a detail further.

[0011] In 10l. polymerization container made from stainless steel which has example 1 churning equipment, a thermometer, and a nitrogen gas introduction pipe the water 140 weight section – teaching – polyvinyl alcohol (the Kuraray make – Kuraray poval PVA-235 and the 88% of the degrees of saponification) After dissolving the 20-degree C viscosity of about 90cps 0.33 weight section (0.55 % of the weight of opposite monomers), and a copper sulfate and the 5 hydrate 0.012 weight section (about 3.6 % of the weight of pair PVA(s)), While adding the methyl methacrylate 60 weight section in which the benzoyl peroxide 0.6 weight section was dissolved and agitating at a fixed churning rotational frequency slowly It heated at 75 degrees C for 5 hours, and the suspension polymerization was completed. After centrifugal hydroextraction, rinsing dryness was carried out and it considered as the product. The obtained particle was screened and it classified by law. Weight % to the particle of the classified whole particle was shown in Table 1. Consequently, in the conventional suspension polymerization, the large drop radial ball child who was not obtained was able to be manufactured with sufficient yield.

[0012] Except having changed composition of example 2 suspension-polymerization liquid into composition of the methyl methacrylate 95 weight section and the ethylene glycol dimethacrylate 5 weight section, the suspension polymerization as well as an example 1 was performed, and the polymer particle of a methacrylic ester was obtained. The obtained polymer particle was screened

and it classified by law. Weight % to the particle of the classified whole particle was shown in Table 1. Consequently, in the conventional suspension polymerization, the large drop radial ball child who was not obtained was able to be manufactured with sufficient yield.

[0013]

[Table 1]

	※ 粒 径				
	1000 $\mu\text{m}$ 以 上	1000 $\mu\text{m}$ ～710 $\mu\text{m}$	710 $\mu\text{m}$ ～500 $\mu\text{m}$	500 $\mu\text{m}$ ～250 $\mu\text{m}$	250 $\mu\text{m}$ 以 下
実施例 1	14.4	31.5	27.3	24.5	2.3
実施例 2	12.2	32.7	30.8	22.3	2.0

※各粒径欄に記載した数値は、重量%を示す。

[0014] Except not adding example of comparison 1 copper sulfate, and 5 hydrate, the suspension polymerization as well as an example 1 was performed, and the polymer particle of a polymethylmethacrylate was obtained. The obtained polymer particle was screened and it classified by law. Weight % to the particle of the classified whole particle was shown in Table 2. Consequently, the obtained polymer particle was far from the large drop radial ball child for whom this invention persons ask, and its yield was also extremely bad.

[0015] As example of comparison 2 water-soluble mineral salt, instead of a copper sulfate and 5 hydrate, the suspension polymerization as well as an example 1 was performed, and the polymer particle of a polymethylmethacrylate was obtained except being metal mol conversion and having carried out equivalent addition of the magnesium sulfate. The particle size distribution of the obtained polymer particle were shown in Table 2. Consequently, the obtained polymer particle was far from the large drop radial ball child for whom this invention persons ask, and its yield was also extremely bad.

[0016]

[Table 2]

	※ 粒 径				
	1000 $\mu\text{m}$ 以 上	1000 $\mu\text{m}$ ～710 $\mu\text{m}$	710 $\mu\text{m}$ ～500 $\mu\text{m}$	500 $\mu\text{m}$ ～250 $\mu\text{m}$	250 $\mu\text{m}$ 以 下
比較例 1	0.0	0.6	6.1	18.2	75.1
比較例 2	0.0	1.1	6.4	22.2	70.3

※各粒径欄に記載した数値は、重量%を示す。

[0017]

[Effect of the Invention] this invention can obtain the polymer particle of the methacrylic ester which comes out spherically [ true ], and has particle size distribution while particle size is 250 micrometers - 2mm with sufficient yield.

[Translation done.]